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Trudy Moskovskogo Neftyanogo Instituta imeni Akademika I. M. Gubkina, 1920 - 1945, Issue 5 (Anniversary Issue), edited by Topchiyev et al., pp 333-335

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AROMATIZATION AND CATALYTIC CRACKING IN THE PRESENCE OF OXIDANTS

G. M. Tsiguro

The catalytic processes represent the greatest accomplishment among the processes applied at present in refining crude oil, but many of them still require substantial improvement. Catalytic cracking installations are extremely complex because of the necessity of periodical regeneration of the catalyst which cokes during the process. The cracking process takes only 10 minutes out of the 30 minutes of the total duration of the operation cycle of the catalytic chamber in the Houdry process. The rest of the time (66%) is spent in operations connected with the regeneration of the catalyst (burning out of the coke). Catalytic aromatization installations are just as complex because of the necessity of carrying out periodic regeneration of the catalyst, a process which consumes 50% of the operating time of the catalyst chamber. Increase of the efficiency of catalytic cracking plants and aromatization installation is very closely connected with the development of conditions under which a minimum of coke precipitation on the catalyst will take place.

One of the methods which allows reducing the deposition of coke on the catalyst is the introduction into the reaction mixture of mild oxidants capable of oxidizing the carbon deposited on the catalyst. Carbon dioxide and steam were investigated in this proposed operation. The use of steam in technical processes meets with difficulties because of the increased corrosion of the walls of the reaction chamber and of some other parts of the apparatus.

We investigated the process of aromatization of n-pentane and of gasolines with a high content of paraffinic hydrocarbons. In the normal procedure, the chromium catalyst has to be regenerated after 2 hours of operation; this regeneration takes about 2 hours. Aromatization in the presence of mild oxidants reduces the deposition of coke on the catalyst and increases the time of effective contact 8 to 10 times. Under the new procedure, this 2-hourly regeneration need only be carried out after 16 to 20 hours of operation of the catalyst. The efficiency of aromatization installations can be increased by 80 percent with this new method.

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In the work, the effect of the chemical nature of the carrier on the activity of the chromium catalyst was clarified. Chromium oxide on a neutral support is the most active; carriers with basic characteristics make for less active catalysts; and chromium oxide deposited on an acidic carrier is the least active. Amphoteric oxides of elements of the third group are more suitable as chromium catalyst carriers than amphoteric oxides of the elements of the sixth group in the periodic system.

The catalytic cracking process with aluminum silicate catalysts can be regulated by changing the physicochemical conditions of the hydrocarbon splitting.

The basic parameters which affect the cracking process are: (1) the length of the period of operation of the catalyst between regenerations, i.e., the time during which it is exposed to the flow of crude material, (2) volumetric rate of flow, (3) the temperature at which the process of splitting of hydrocarbons is accomplished, (4) the pressure used in the cracking process, and (5) the activity of the catalyst. The most effective conditions for cracking are created during the shortest periods of operation of the catalyst, i.e., during the first minutes of operation of the catalyst after its regeneration.

The catalyst carries the process of splitting of hydrocarbons furthest when it is least poisoned by coke deposits. Increased activity of the catalyst sets up the conditions for an increased degree of cracking and a more thorough decomposition of the hydrocarbons, characterized by increased formation of gaseous hydrocarbons and increased deposition of coke. The deposition of coke on the surface of the catalyst proceeds much more intensively in the first minutes of operation of the catalyst, and subsides rapidly as the operation continues. The first active centers to be poisoned and to go out of action are those which exercised the most intensive control over the process. Thus it is shown that the active centers on the surface of the catalyst differ in regard to their activity. The rate of drop of the activity of the catalyst, observed at long intervals, depends on the initial activity of the catalyst, the number of regenerations carried out, the character of the raw material being treated, and the thoroughness with which the regenerations are carried out.

Under very severe conditions of hydrocarbon decomposition, increased coke formation and gas formation lead to a reduced yield of gasoline as compared with the possible maximum. The yield of gasoline varies with the degree of severity of conditions, passing through a maximum corresponding to the optimum activity of the catalyst. From theoretical considerations follows the experimentally confirmed consequence that light products are more difficult to crack and require higher catalyst activity, higher temperature, the use of a lower volumetric rate of flow of the raw material being catalyzed, and higher pressure in order to obtain high yields of gasoline. Cracking of heavy crude materials requires lower pressure, so that the deposition of coke can be kept at the normal level (approximately 7 grams per liter of catalyst during the first 10 minutes after regeneration). This can be accomplished easily by adding carbon dioxide or steam to the material to be cracked in order to reduce the partial vapor pressure of the petroleum product below atmospheric pressure; the carbon dioxide and the steam act as oxidants at the same time and reduce the deposition of coke.

The coke deposit on the catalyst, expressed in grams per liter, does not depend on the volumetric rate of flow of the input of raw material for cracking, if all other conditions remain constant. The increase of coke deposit is thus a function of the quantity of raw material being treated.

Investigation of the Houdry catalytic cracking process with the use of mild oxidants (carbon dioxide, steam) showed that it is possible to lengthen the contact period considerably and at the same time to reduce the coke

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deposition on the catalyst. In addition, heavy material of increased specific weight can be successfully treated in the process. In industrial practice, catalyst regeneration gases and furnace gases can be used for this purpose. The method proposed by us allows considerable increases in the efficiency of catalytic cracking installations.

The content of aromatic hydrocarbons in gasoline obtained according to our process is somewhat higher than usual.

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